N.A.M. ten Asbroek

CO_2 removal using membrane gas absorption

TNO Environment, Energy and Process Innovation

TNO Environment, Energy and Process Innovation (TNO-MEP)
Department of Chemical Engineering
e-mail: N.A.M.tenAsbroek@mep.tno.nl
Internet: www.mep.tno.nl

Overview

- Introduction of TNO
- TNO R&D programme (flue gas decarbonisation)
- Membrane gas absorption technology
- Experimental results
- Applications
- CASTOR project
- Conclusion

TNO is active in five core areas

Quality of life

Defence and public safety

Advanced products, processes and systems

Natural and built environment

ICT and services

TNO projects on Carbon capture and storage.

- **TNO-MEP (Environment, Energy and Process innovation)**
  - Supercritical water gasification (SWG) → Super Diesel project (nl.)
  - Chemical looping combustion (CLC) → ENCAP/CATO (eu./nl.)
  - Membrane gas absorption (MGA) → CASTOR/CATO (eu./nl.)

- **TNO-TPD**
  - Oxygen transport membranes → CASTOR/CATO (eu./nl.)

- **TNO-NITG (Netherlands Institute of Applied Geoscience)**
  - CO_2 storage → CASTOR/CATO (eu./nl.)

TNO-MEP R&D programme on CO_2 membrane technology for flue gases

- **Development of absorption process through novel absorption liquids (CORAL):**

  1. Membrane contactors

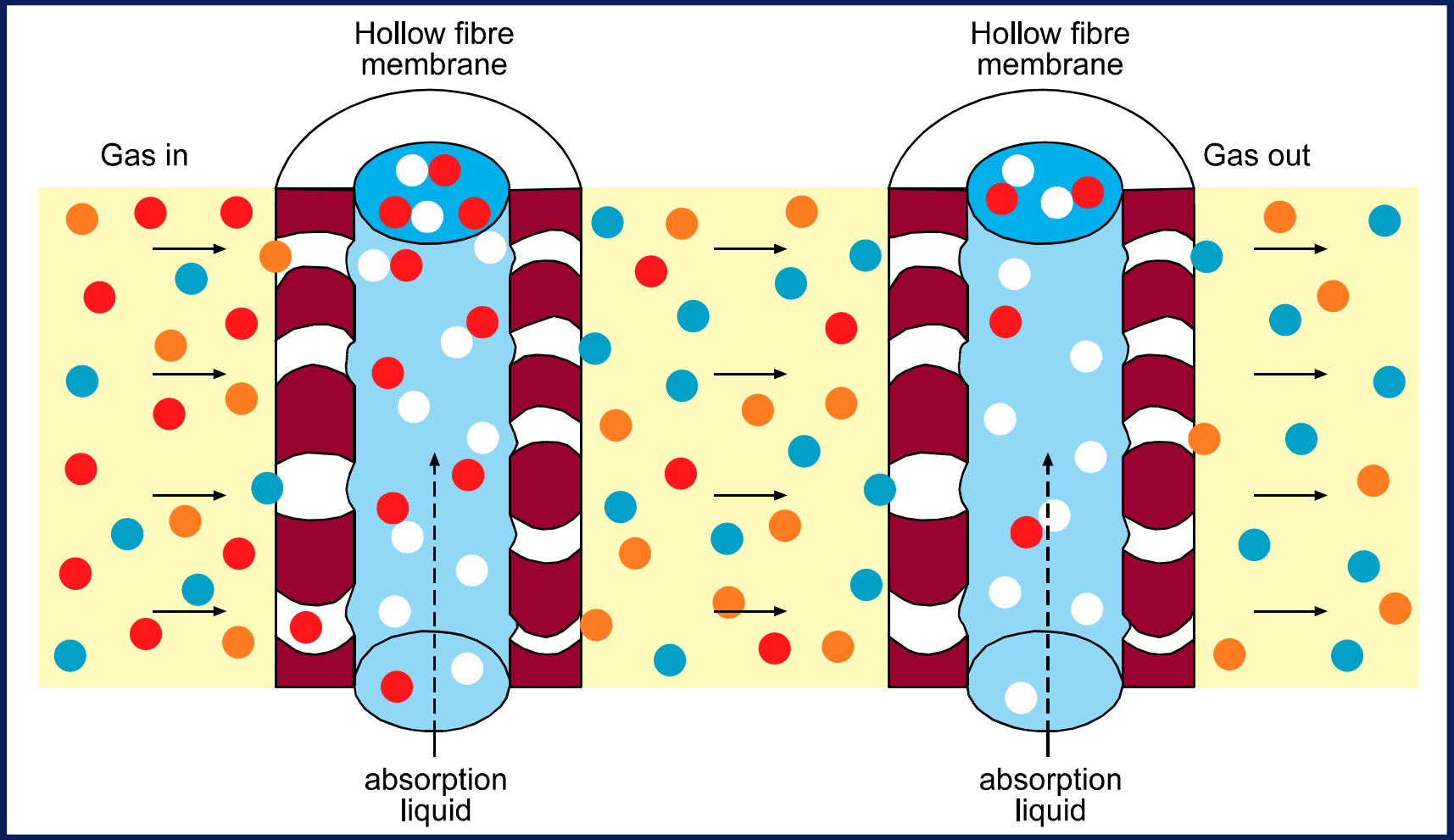
  - Combination of selectivity of absorption processes with flexibility of membrane processes into superior process (MGA)

  2. DECAB

  - High loading at low CO_2-partial pressure using conventional contactors and crystallising solutions

- **Fundamental research on absorption processes for gas treatment in centre of separation technology (University Twente)**

Principle CO_2 Membrane Gas Absorption



CO_2, present in the flue gas, is selectively absorbed into a proprietary absorption liquid through a porous membrane

Advantages MGA vs conventional absorber

- High selectivity
- Compact equipment
- Independent flow control
- No entrainment, flooding, channelling, foaming
- Not influenced by tilt
- Low liquid pumping power
- Flexibility in scale-up

Novel absorption liquids: CORAL

- **CORAL = $\underline{CO_2}$-$\underline{R}$emoval $\underline{A}$bsorption $\underline{L}$iquid**
  - Mixtures of amino-acids, alkali salts and amines
- **CORAL vs MEA in MGA**
  - Stable operation with polyolefin membranes
  - Better oxygen stability
  - Less corrosive
  - No losses of active components
  - High thermal stability

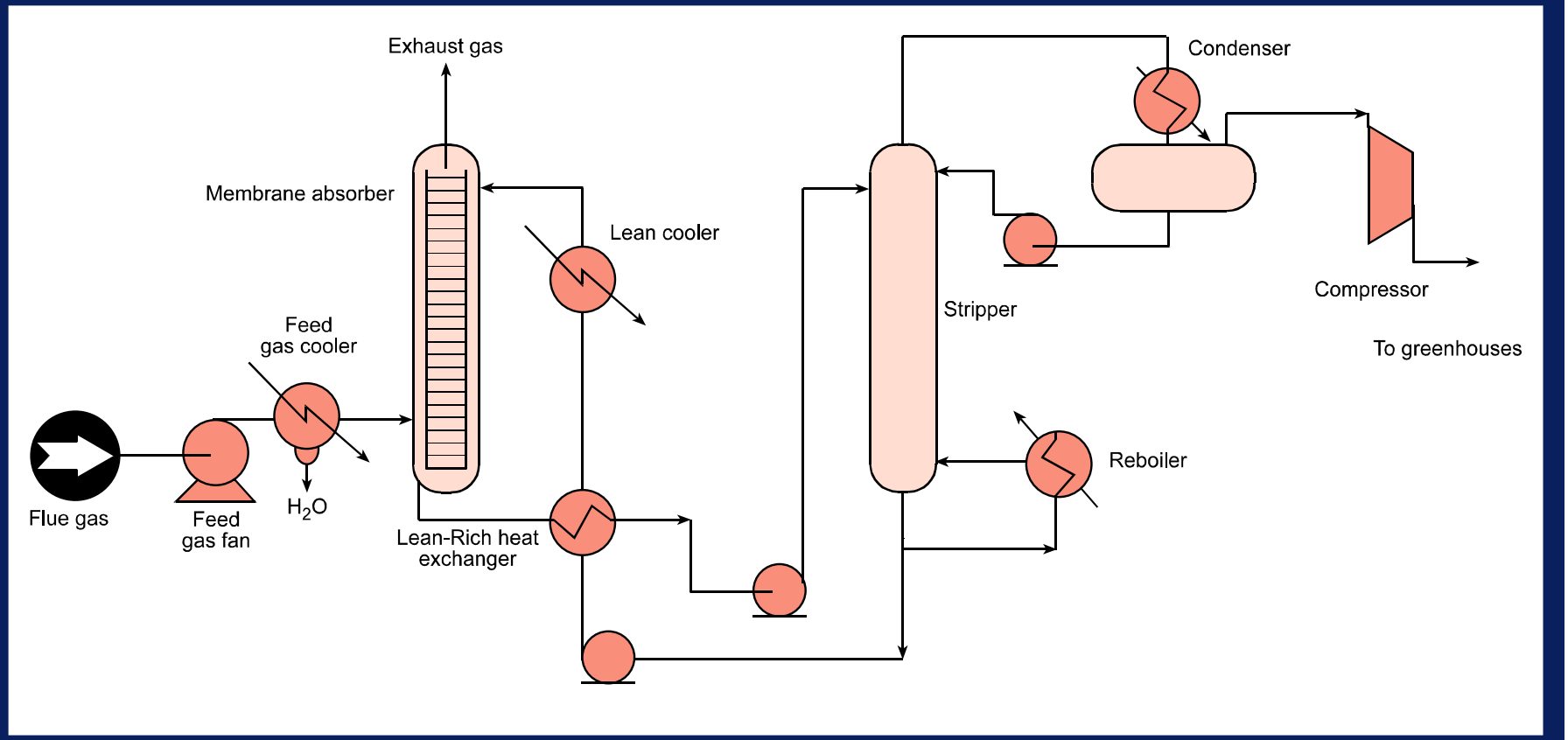
CORAL vs MEA
Comparison of characteristics

Property	MEA	CORAL
2nd order reaction rate constant at 295 K	5.7 m^3/mol·s	12.6 m^3/mol·s
Specific absorption liquid flow	15-25 m^3/tonne CO_2	20 m^3/tonne CO_2
CO_2 binding energy	1.7 GJ/tonne CO_2	1.4 GJ/tonne CO_2

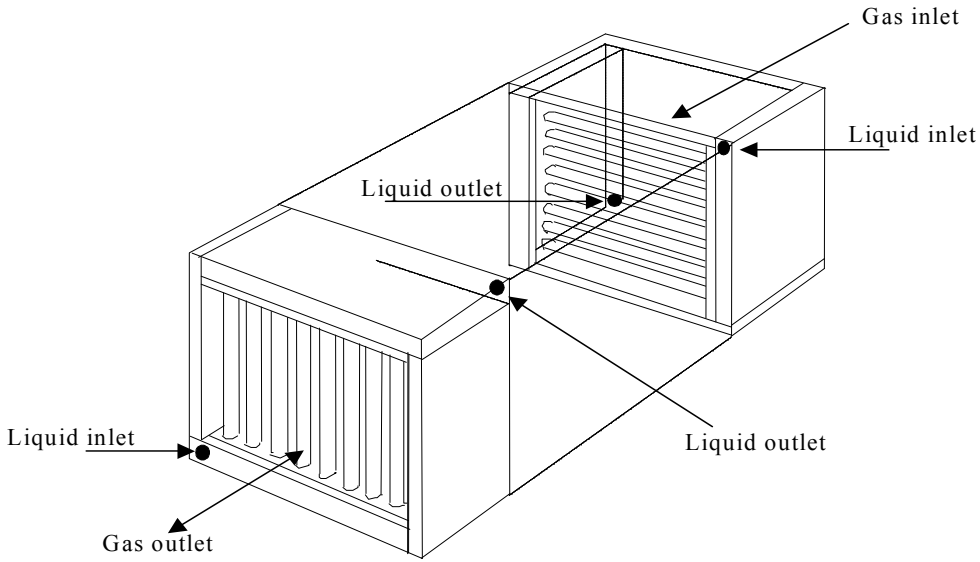
Overview past/current activities for CO_2-capture using membrane gas absorption

- **Assessment studies (1991-present)**
- **Development of MGA for NL horticultural industry (1993-present)**
- **TNO-MGA patent; USA (1998), Europe (2001)**
- **Various spin-off projects:**
  - Ammonia MGA (commercial application, Kirkpatrick Honor Award 2001)
  - Spacecrafts (demonstrator tested)
  - Fuel cells (prototype undergoing testing)
  - Submarines (prototype under construction)
  - Medical application (project development)
- **CASTOR (2004)**

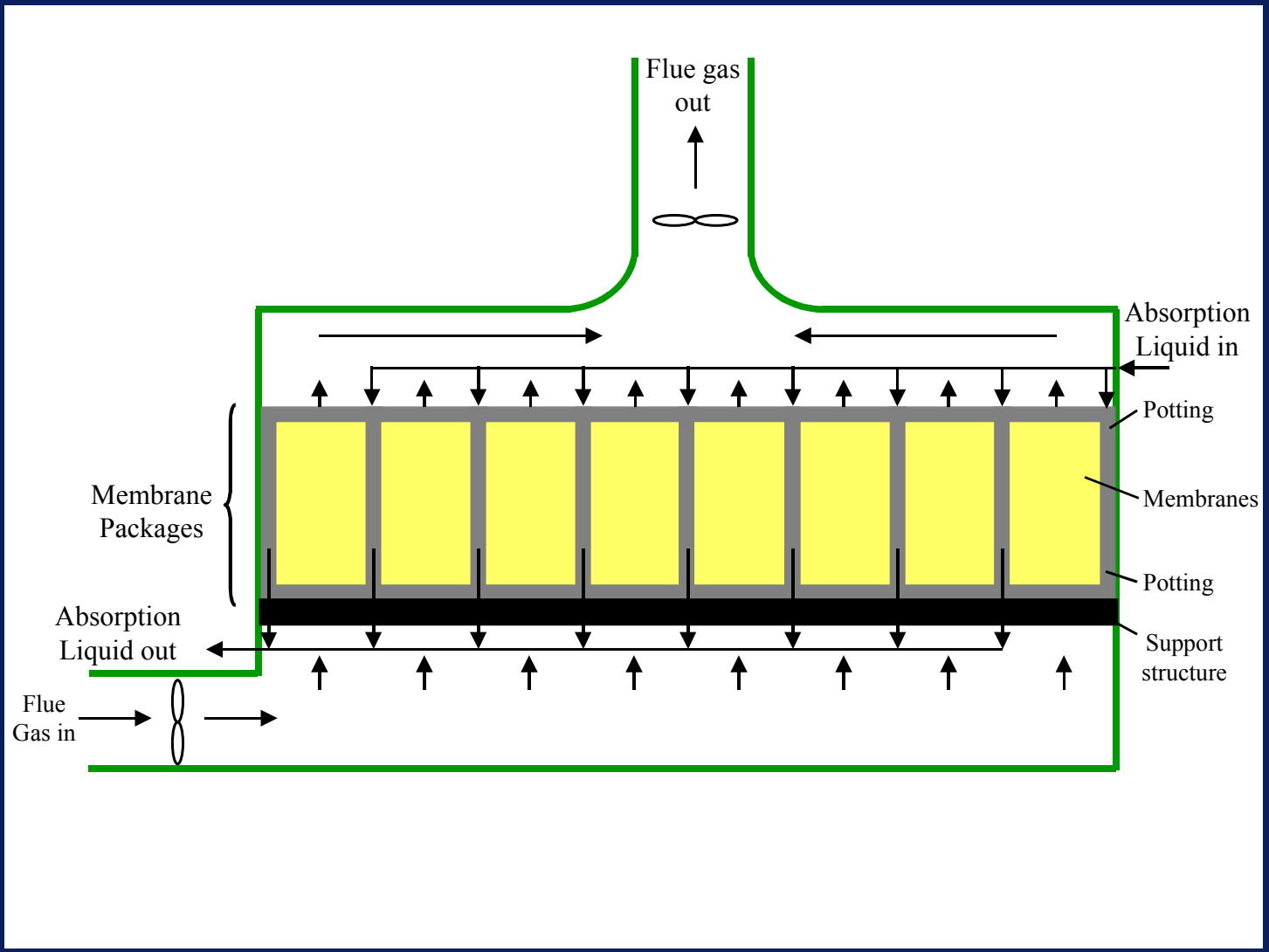
CO_2-MGA-Flowsheet



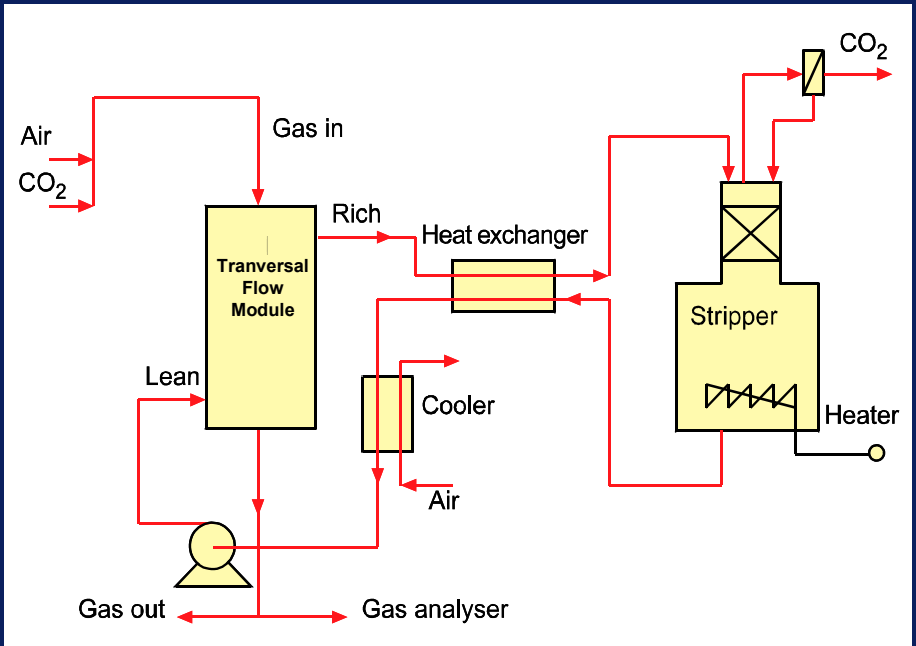
Alternative module design: Transversal flow module



Scale-up of MGA modules



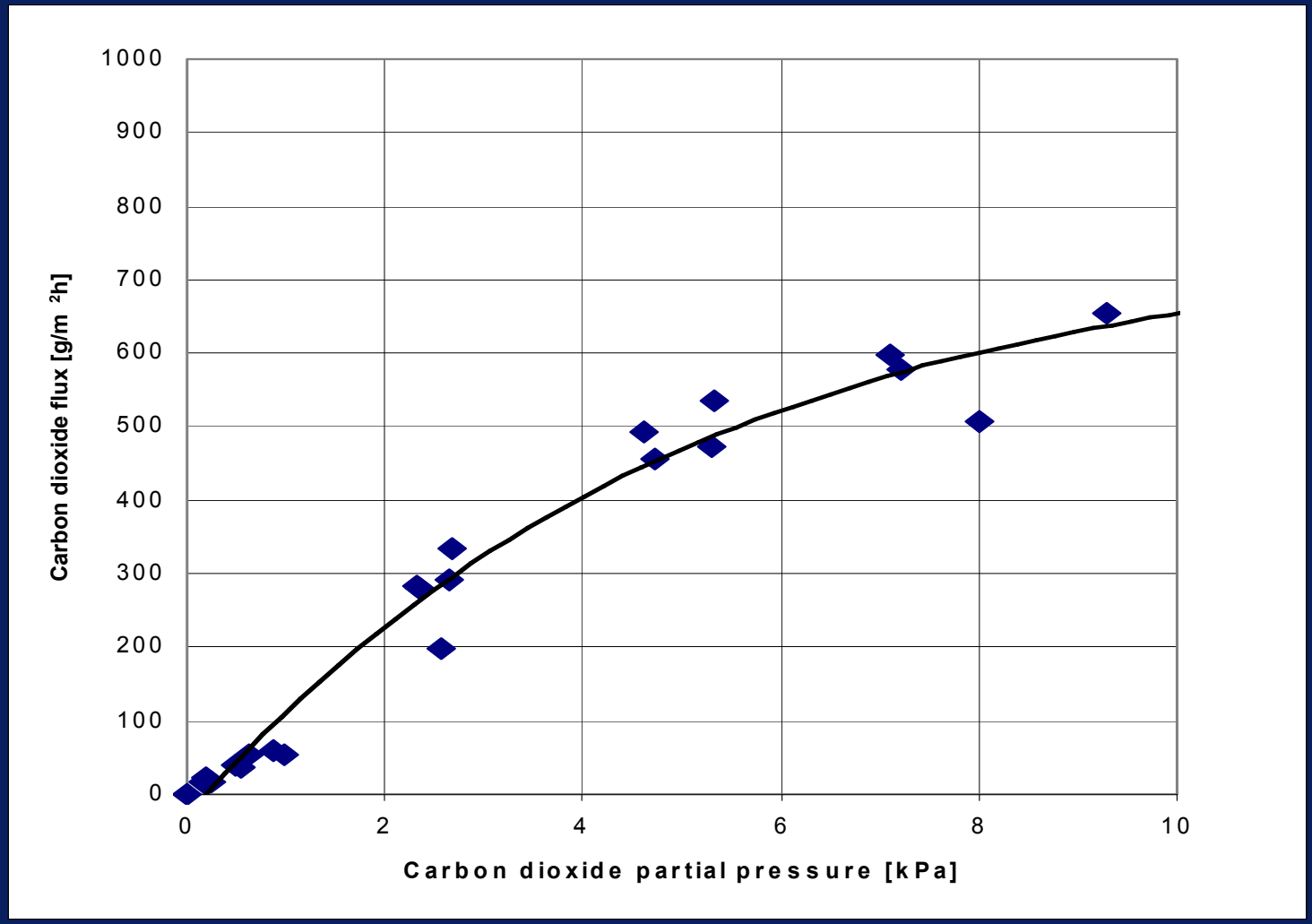
CO_2-MGA bench scale set-up



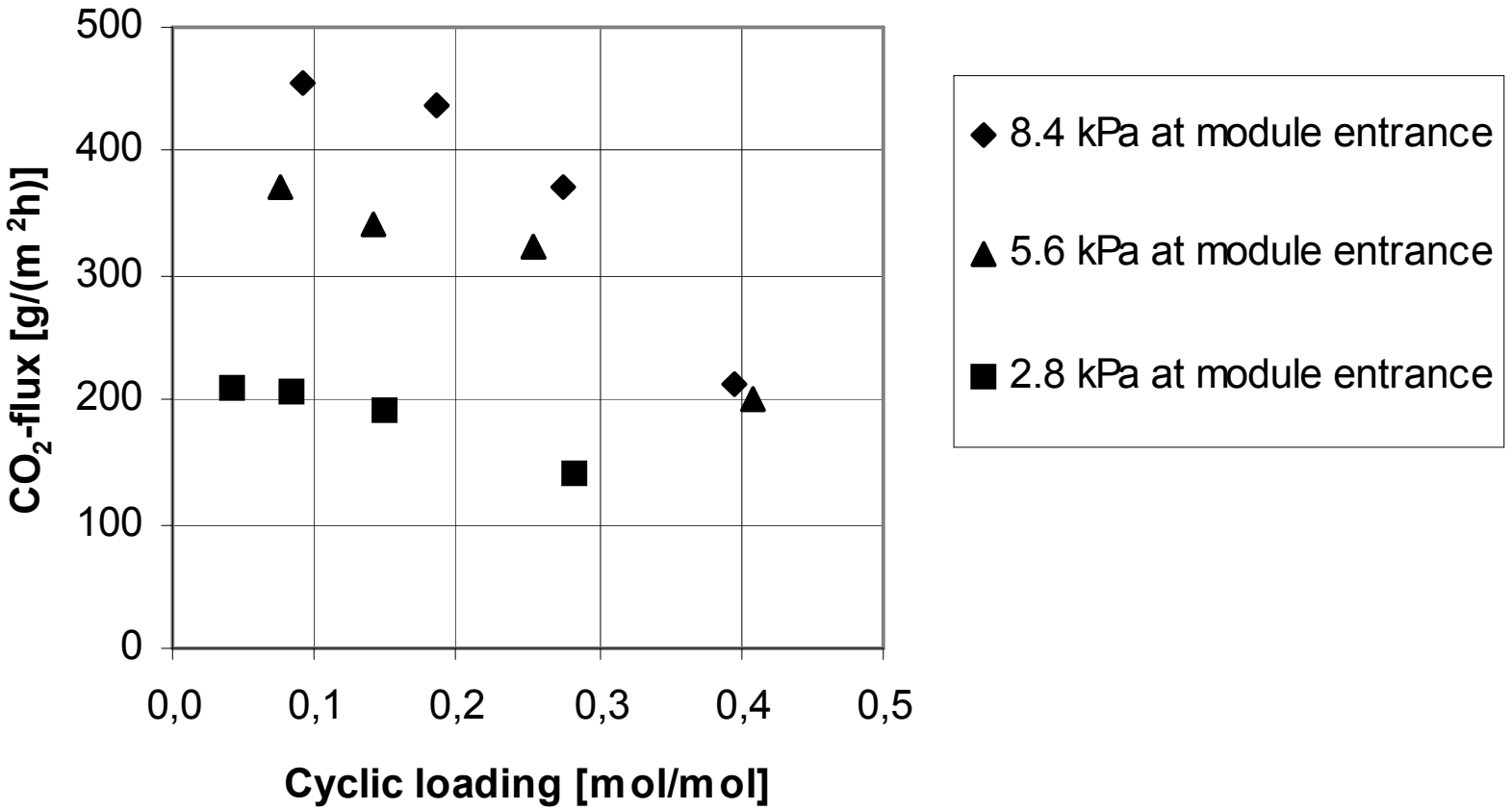
Specifications

- Gas flow 0.5 - 4 m^3/h
- Liquid flow 0.5 - 20 l/h
- CO_2-content feed 0.5 - 10 %
- Membrane area 0.27 m^2
- Membranes Polypropylene
- Modules Transversal flow
- No. of elements 4
- Flow pattern Counter-current
- Regeneration 105 °C

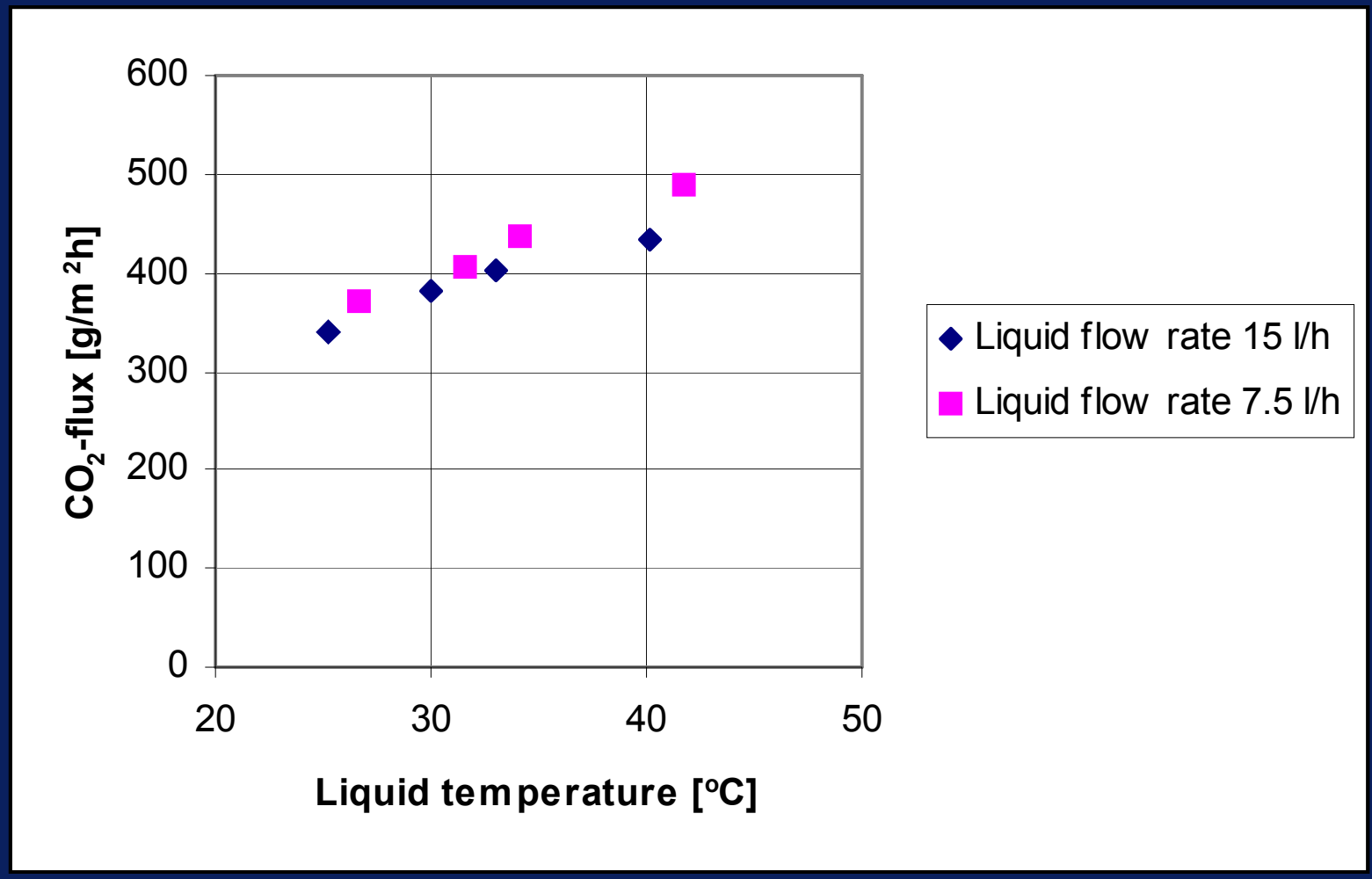
Experimental results with bench-scale set-up
Influence of CO_2-content in feed gas



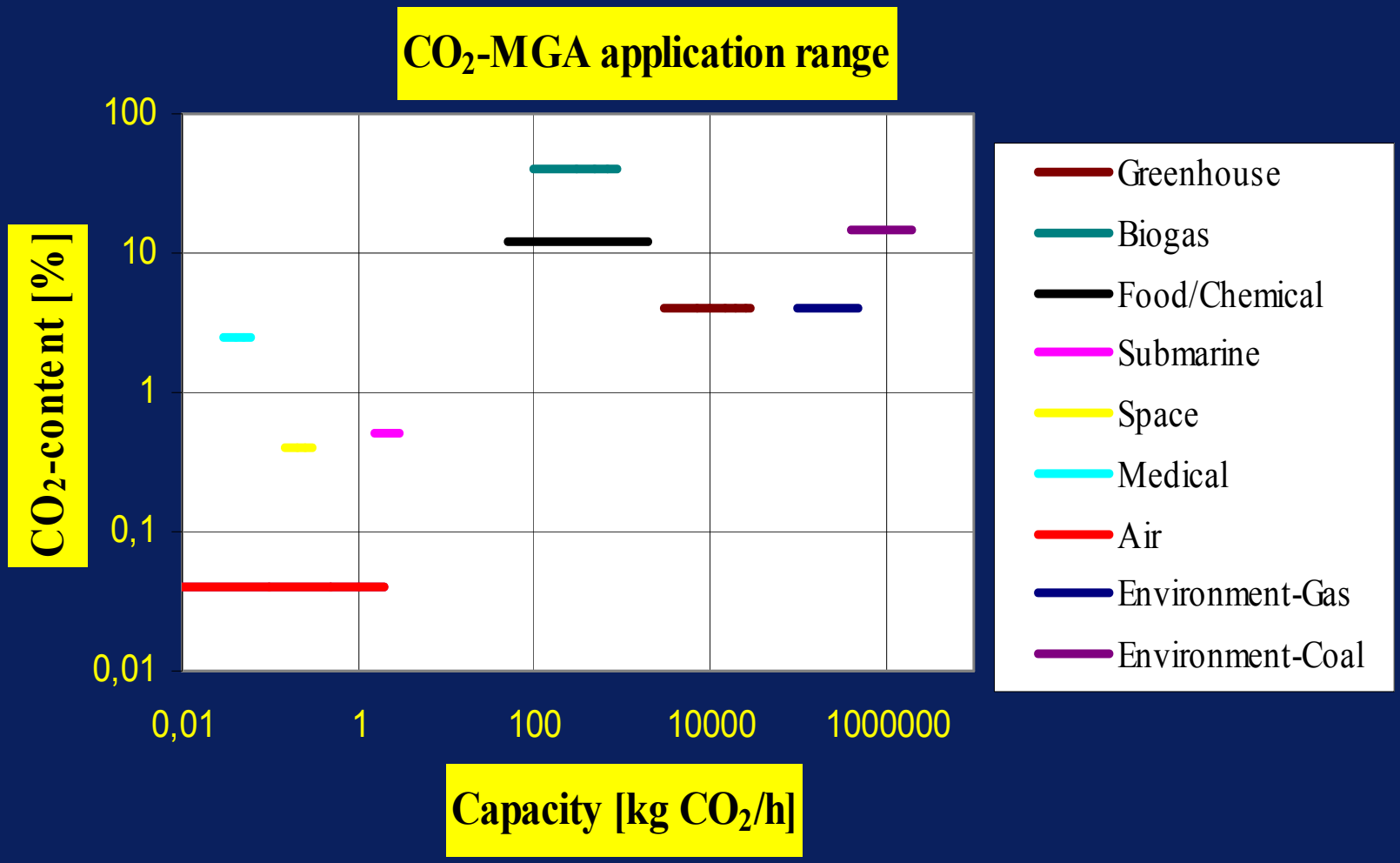
Experimental results with bench-scale set-up
Influence of cyclic loading



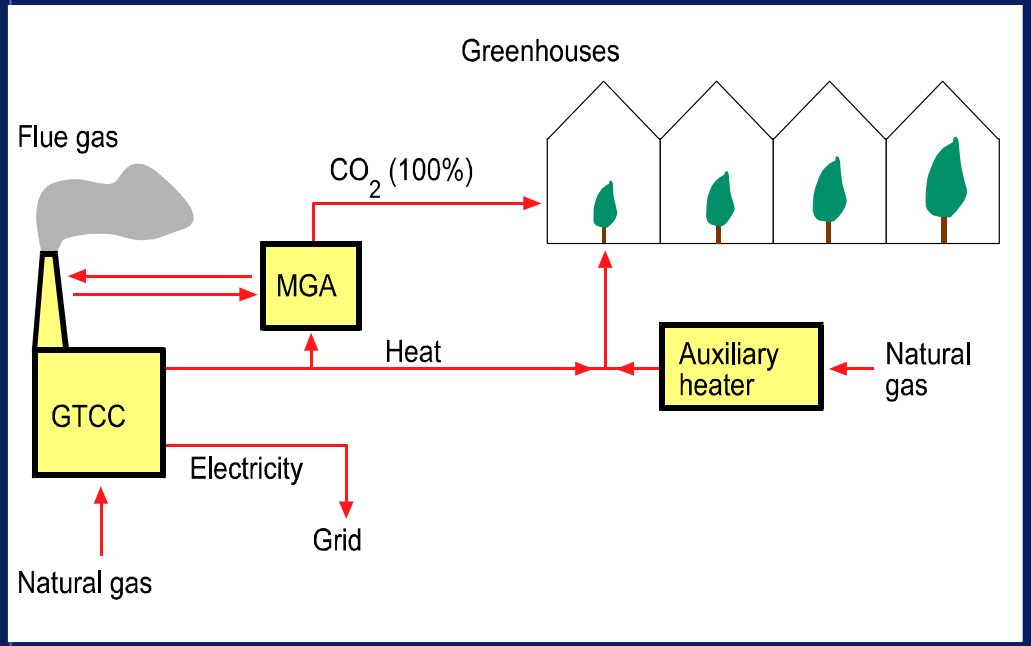
Experimental results with bench-scale set-up
Influence of liquid temperature



Opportunities for CO_2-MGA: Customer driven developments



CO_2-production for greenhouses



- CO_2-production gives production increase
- CO_2-demand and heat demand are anticyclic
- Energy efficient integration of CO_2/heat supply

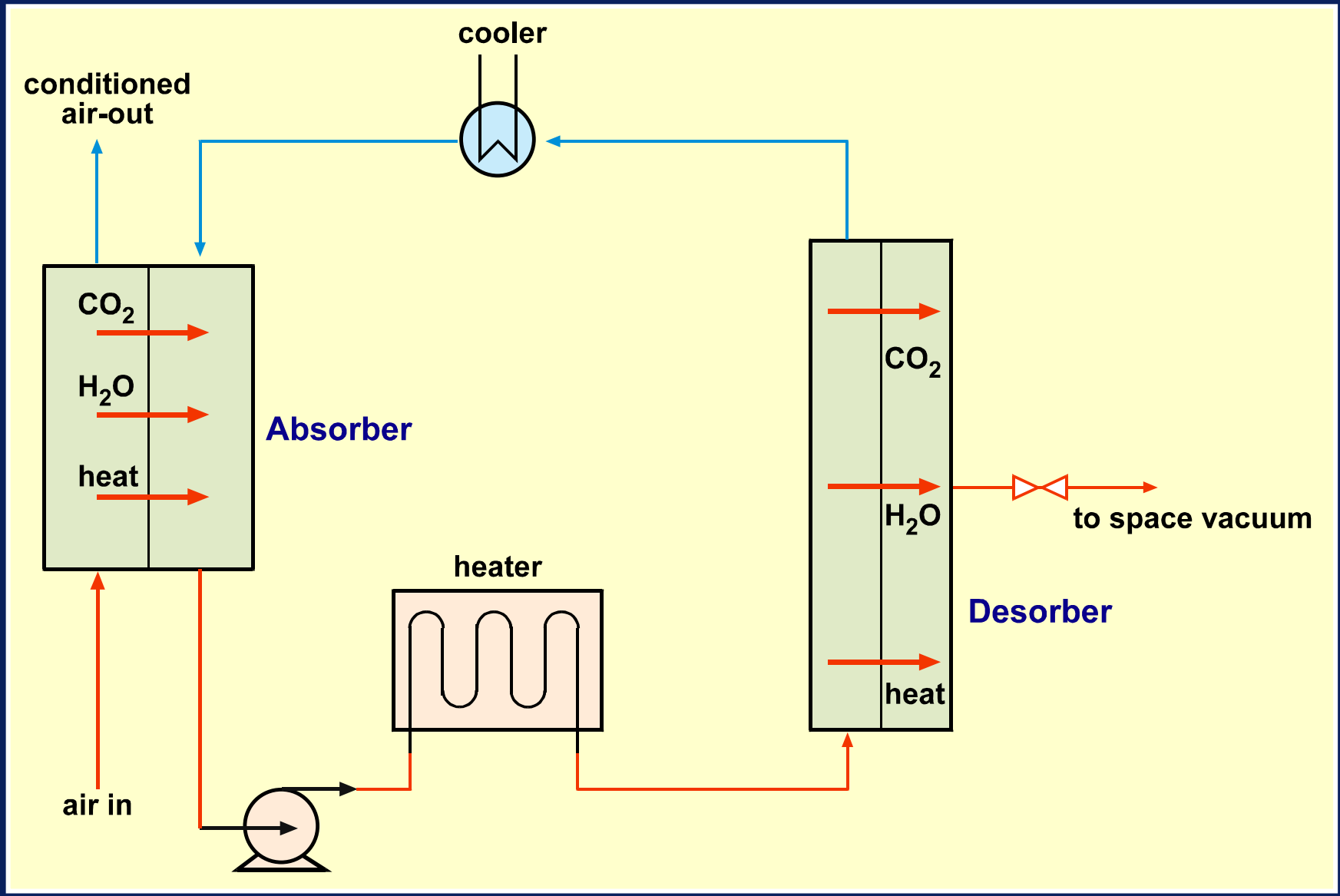
Pilot plant at power station RoCa 3 (NL)

The process has been investigated and demonstrated using a pilot plant on a site in The Netherlands

Spacecrafts: Control of CO_2, H_2O and temperature

- **Indoor climate control**
- **Membrane absorption and desorption**
- **Demonstrator at one astronaut scale**
  - CO_2 level at 0.5%
  - CO_2 removal: 40 g/h
  - Feed gas: 30 m^3/h
- **Porous polypropylene membranes**
- **Cross-flow membrane absorber at room temperature**
  - Membrane area: 4 m^2
- **Conventional membrane desorber at 40 °C**
  - Membrane area: 40 m^2

Principle Membrane Gas Absorption/Desorption



Alkaline fuel cells: CO_2 removal from Air

- **Maintaining CO_2-levels below 50 ppm**
- **Conventional flow sheet with thermal regeneration**
- **Demonstrator at fuel cell scale**
  - CO_2 level at 50 ppm
  - CO_2 removal: 40 g/h
  - Feed gas: 45 m^3/h
- **Porous polypropylene membranes**
- **Cross-flow membrane absorber at room temperature**
  - Membrane area: 100 m^2

EU 6th framework program: CASTOR

Reducing cost of CO_2 absorption processes by 50%

- From € 50/tonne CO_2 ($60) to € 25/tonne CO_2 ($30)

- **Improving absorption liquid**
  - Low regeneration energy
  - High loading
  - Low operating costs
- **Improving membrane modules for absorption/desorption**
  - Cheap membranes
  - Low module fabrication costs
  - Modular design
- **Lowering plant design and building costs**
  - Modular building blocks

Conclusions

- Membrane gas absorption provides efficient way for carbon dioxide recovery/removal
- CORAL liquids are excellent alternatives to available absorption liquids (reactivity, loading, stability)
- Niche-applications can be developed rapidly
- Scale-up of process and membrane modules is crucial item for large applications